

D20
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



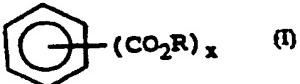
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C10L 1/18, 1/22	A1	(11) International Publication Number: WO 95/29973 (43) International Publication Date: 9 November 1995 (09.11.95)
(21) International Application Number: PCT/US95/04924 (22) International Filing Date: 24 April 1995 (24.04.95)		(81) Designated States: AU, CA, CN, JP, KR, NZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(30) Priority Data: 08/236,734 2 May 1994 (02.05.94) US		Published <i>With international search report.</i>
(71) Applicant: CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).		
(72) Inventors: ANSARI, Mathew, H.; 882 - 26th Avenue, San Francisco, CA 94121 (US). CHERPECK, Richard, E.; 8962 Cypress Avenue, Cottati, CA 94931 (US). CHEVALIER, Randy, G.; 3115 Ellis Street, Berkeley, CA 94703 (US). TOMAN, Jeffrey, J.; 5430 Proctor Avenue, Oakland, CA 94618 (US).		
(74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		

(54) Title: **FUEL ADDITIVE COMPOSITIONS CONTAINING AN ALIPHATIC AMINE, A POLYOLEFIN AND AN AROMATIC ESTER**

(57) Abstract

A fuel additive composition comprising:
a) a fuel-soluble aliphatic hydrocarbyl-substituted amine having at least one basic nitrogen atom wherein the hydrocarbyl group has a number average molecular weight of about 700 to 3,000; b) a polyolefin polymer of a C₂ to C₆ monoolefin, wherein the polymer has a number average molecular weight of about 350 to 3,000; and c) an aromatic di- or tri-carboxylic acid ester of formula (I), wherein R is an alkyl group of 4 to 20 carbon atoms, and x is 2 or 3.



BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Larvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

WO 95/29973

-1-

01 FUEL ADDITIVE COMPOSITIONS CONTAINING
02 AN ALIPHATIC AMINE, A POLYOLEFIN
03 AND AN AROMATIC ESTER

04 BACKGROUND OF THE INVENTION

05
06
07 This invention relates to a fuel additive composition. More
08 particularly, this invention relates to a fuel additive
09 composition containing an aliphatic amine, a polyolefin and
10 an aromatic ester.

11
12 It is well known that automobile engines tend to form
13 deposits on the surface of engine components, such as
14 carburetor ports, throttle bodies, fuel injectors, intake
15 ports and intake valves, due to the oxidation and
16 polymerization of hydrocarbon fuel. These deposits, even
17 when present in relatively minor amounts, often cause
18 noticeable driveability problems, such as stalling and poor
19 acceleration. Moreover, engine deposits can significantly
20 increase an automobile's fuel consumption and production of
21 exhaust pollutants. Therefore, the development of effective
22 fuel detergents or "deposit control" additives to prevent or
23 control such deposits is of considerable importance and
24 numerous such materials are known in the art.

25
26 For example, U.S. Patent No. 3,438,757 to Honnen et al.
27 discloses branched chain aliphatic hydrocarbon N-substituted
28 amines and alkylene polyamines having a molecular weight in
29 the range of about 425 to 10,000, preferably about 450 to
30 5,000, which are useful as detergents and dispersants in
31 hydrocarbon liquid fuels for internal combustion engines.

32
33 U.S. Patent No. 3,502,451 to Moore et al. discloses motor
34 fuel compositions containing a polymer or copolymer of a C₂

-2-

01 to C₆ unsaturated hydrocarbon or the corresponding
02 hydrogenated polymer or copolymer, wherein the polymer or
03 copolymer has a molecular weight in the range of about 500
04 to 3,500. This patent further teaches that polyolefin
05 polymers of propylene and butylene are particularly
06 preferred.

07
08 U.S. Patent No. 3,700,598 to Plonsker et al. discloses
09 lubricating oil and fuel compositions containing a small
10 amount of an N-hydrocarbyl-substituted nitrilotris
11 ethylamine, wherein the hydrocarbyl group is preferably a
12 polyolefin group having a molecular weight of about 300 to
13 20,000, preferably from 500 to 2,000. This patent further
14 teaches that fuel compositions containing this additive will
15 preferably also contain a small amount of a mineral oil
16 and/or a synthetic olefin oligomer having an average
17 molecular weight of about 300 to 2,000.

18
19 U.S. Patent No. 3,756,793 to Robinson discloses a fuel
20 composition containing minor amounts of (A) a polyamine
21 which is the reaction product of a halohydrocarbon having an
22 average molecular weight between 600 to 2500 and an alkylene
23 polyamine, and (B) an organic substance having a viscosity
24 between 20 and 2500 cs. at 20°C. This patent further
25 discloses that a wide variety of compounds are suitable as
26 the organic substance, including polyamines, amides, and
27 esters or mixtures of esters, such as aliphatic diesters of
28 dibasic aliphatic carboxylic acids. Preferred materials for
29 use as the organic substance are described in this patent as
30 polymers or copolymers having an average molecular weight of
31 300 to 5,000 which are selected from hydrocarbons,
32 substituted hydrocarbons containing oxygen and substituted
33 hydrocarbons containing oxygen and nitrogen. Most preferred

34

-3-

01 polymeric compounds are described in this patent as
02 polyalkylene oxides and polyether glycols.

03
04 U.S. Patent No. 4,173,456 to Scheule et al. discloses a fuel
05 additive composition comprising (A) a hydrocarbon-soluble
06 acylated poly(alkyleneamine) and (B) a normally liquid
07 hydrocarbon-soluble polymer of a C₂ to C₆ olefin, wherein
08 the polymer has an average molecular weight of about 400 to
09 3,000.

10
11 U.S. Patent No. 4,357,148 to Graiff discloses a motor fuel
12 composition containing an octane requirement
13 increase-inhibiting amount of (a) an oil soluble aliphatic
14 polyamine containing at least one olefinic polymer chain and
15 a molecular weight of about 600 to 10,000 and (b) a polymer
16 and/or copolymer of a monoolefin having 2 to 6 carbon atoms,
17 wherein the polymer has a number average molecular weight of
18 about 500 to 1500.

19
20 U.S. Patent No. 4,832,702 to Kummer et al. discloses a fuel
21 or lubricant composition containing one or more polybutyl or
22 polyisobutylamines. This patent further discloses that,
23 since, in fuel additives, about 50% by weight of the active
24 substance can be replaced by polyisobutene without loss of
25 efficiency, the addition of polyisobutene having a molecular
26 weight of 300 to 2000, preferably from 500 to 1500, is
27 particularly advantageous from the point of view of cost.

28
29 U.S. Patent No. 5,004,478 to Vogel et al. discloses a motor
30 fuel for internal combustion engines which contains an
31 additive comprising (a) an amino- or amino-containing
32 detergent and (b) a base oil which is a mixture of (1) a
33 polyether based on propylene oxide or butylene oxide and
34

-4-

01 having a molecular weight not less than 500, and (2) an
02 ester of a monocarboxylic or polycarboxylic acid and an
03 alkanol or polyol.

04 U.S. Patent No. 5,089,028 to Abramo et al. discloses a fuel
05 composition containing an additive which comprises the
06 combination of (1) a polyalkenyl succinimide, (2) a
07 polyalkylene polymer, such as polyisobutylene or
08 polypropylene, (3) an ester of an aliphatic or aromatic
09 carboxylic acid, and (4) a polyether, such as polybutylene
10 oxide, polypropylene or a polybutylene/polypropylene
11 copolymer. The additive may also contain an optional amount
12 of a mineral oil or a synthetic oil.

14 U.S. Patent No. 5,242,469 to Sakakibara et al. discloses a
15 gasoline additive composition comprising (A) a monoester,
16 diester or polyolester, and (B) a dispersant selected from
17 (1) a monosuccinimide, (2) a bis-succinimide, (3) an
18 alkylamine having a polyolefin polymer as an alkyl group and
19 an average molecular weight of 500-5,000, and (4) a
20 benzylamine derivative having an average molecular weight of
21 500-5,000. The additive composition may additionally
22 contain a polyoxyalkylene glycol or its derivative and/or a
23 lubricant oil fraction.

25 PCT International Patent Application Publication
26 No. WO 92/15656, published September 17, 1992, discloses an
27 additive for gasoline petroleum fuel comprising (A) an oil
28 soluble polyolefin polyamine containing at least one
29 olefinic polymer chain, and (B) a polymer of a C₂ to C₆
30 monoolefin, wherein the polymer has a number average
31 molecular weight of up to 2,000, and preferably up to 500.
32 This document further discloses that the additive may be
33

-5-

01 used in combination with other additives, including
02 plasticizer esters, such as adipates and mixtures thereof,
03 scavengers, antioxidants, ignition improvers, and metal
04 deactivators.

05
06 European Patent Application Publication No. 0,382,159 A1,
07 published August 16, 1990, discloses a liquid hydrocarbon
08 fuel for an internal combustion engine containing a deposit
09 removing and residue inhibiting amount of at least one C₁ to
10 C₄ dialkyl ester of a C₄ to C₆ aliphatic dibasic acid.

11
12 European Patent Application Publication No. 0,356,726 A2,
13 published March 7, 1990 discloses fuel compositions
14 containing esters of aromatic di-, tri-, or tetra-carboxylic
15 acids with long-chain aliphatic alcohols or ether alcohols,
16 wherein the alcohols are produced by the hydroformylation of
17 branched olefins, and wherein the total carbon number of the
18 esters is at least 36 carbon atoms and the molecular weight
19 of the esters is 550 to 1,500, preferably 600 to 1,200.

20
21 U.S. Patent No. 4,877,416 to Campbell discloses a fuel
22 composition which contains (A) a hydrocarbyl-substituted
23 amine or polyamine having an average molecular weight of
24 about 750 to 10,000 and at least one basic nitrogen atom,
25 and (B) a hydrocarbyl-terminated poly(oxyalkylene) monool
26 having an average molecular weight of about 500 to 5,000.

27
28 It has now been discovered that the unique combination of an
29 aliphatic hydrocarbyl-substituted amine, a polyolefin
30 polymer and an aromatic di- or tri-carboxylic acid ester
31 provides excellent valve sticking performance, while
32 maintaining good control of engine deposits, especially

33
34

WO 95/29973

-6-

01 intake valve deposits, when employed as a fuel additive
02 composition for hydrocarbon fuels.

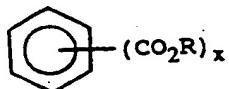
SUMMARY OF THE INVENTION

05 The present invention provides a novel fuel additive
06 composition comprising:

- 08
09 (a) a fuel-soluble aliphatic hydrocarbyl-substituted amine
10 having at least one basic nitrogen atom wherein the
11 hydrocarbyl group has a number average molecular weight
12 of about 700 to 3,000;

13
14 (b) a polyolefin polymer of a C₂ to C₆ monoolefin, wherein
15 the polymer has a number average molecular weight of
16 about 350 to 3,000; and

17
18 (c) an aromatic di- or tri-carboxylic acid ester of the
19 formula:



wherein R is an alkyl group of 4 to 20 carbon atoms,
and x is 2 or 3.

27 The present invention further provides a fuel composition
28 comprising a major amount of hydrocarbons boiling in the
29 gasoline or diesel range and an effective detergent amount
30 of the novel fuel additive composition described above.
31

32

-7-

01 The present invention is also concerned with a fuel
02 concentrate comprising an inert stable oleophilic organic
03 solvent boiling in the range of from about 150°F to 400°F
04 and from about 10 to 70 weight percent of the fuel additive
05 composition of the instant invention.

06 Among other factors, the present invention is based on the
07 surprising discovery that the unique combination of an
08 aliphatic amine, a polyolefin and an aromatic ester provides
09 unexpectedly superior valve sticking performance when
10 compared to the combination of aliphatic amine and either
11 polyolefin or aromatic ester alone, while maintaining good
12 control of engine deposits.
13

14 DETAILED DESCRIPTION OF THE INVENTION
15

16
17 As noted above, the fuel additive composition of the present
18 invention contains an aliphatic hydrocarbyl-substituted
19 amine, a polyolefin polymer, and an aromatic di- or
20 tri-carboxylic acid ester. These compounds are described in
21 detail below.

22
23 A. The Aliphatic Hydrocarbyl-Substituted Amine

24
25 The fuel-soluble aliphatic hydrocarbyl-substituted amine
26 component of the present fuel additive composition is a
27 straight or branched chain hydrocarbyl-substituted amine
28 having at least one basic nitrogen atom wherein the
29 hydrocarbyl group has a number average molecular weight of
30 about 700 to 3,000. Typically, such aliphatic amines will
31 be of sufficient molecular weight so as to be nonvolatile at
32 normal engine intake valve operating temperatures, which are
33 generally in the range of about 175°C to 300°.

34

-8-

01 Preferably, the hydrocarbyl group will have a number average
02 molecular weight in the range of about 750 to 2,200, and
03 more preferably, in the range of about 900 to 1,500. The
04 hydrocarbyl group will generally be branched chain.

05 When employing a branched-chain hydrocarbyl amine, the
06 hydrocarbyl group is preferably derived from polymers of C₂
07 to C₆ olefins. Such branched-chain hydrocarbyl group will
08 ordinarily be prepared by polymerizing olefins of from 2 to
09 6 carbon atoms (ethylene being copolymerized with another
10 olefin so as to provide a branched-chain). The branched
11 chain hydrocarbyl group will generally have at least
12 1 branch per 6 carbon atoms along the chain, preferably at
13 least 1 branch per 4 carbon atoms along the chain and, more
14 preferably, at least 1 branch per 2 carbon atoms along the
15 chain. The preferred branched-chain hydrocarbyl groups are
16 polypropylene and polyisobutylene. The branches will
17 usually be of from 1 to 2 carbon atoms, preferably 1 carbon
18 atom, that is, methyl. In general, the branched-chain
19 hydrocarbyl group will contain from about 18 to about
20 214 carbon atoms, preferably from about 50 to about
21 157 carbon atoms.
22

23
24 In most instances, the branched-chain hydrocarbyl amines are
25 not a pure single product, but rather a mixture of compounds
26 having an average molecular weight. Usually, the range of
27 molecular weights will be relatively narrow and peaked near
28 the indicated molecular weight.

29
30 The amine component of the branched-chain hydrocarbyl amines
31 may be derived from ammonia, a monoamine or a polyamine.
32 The monoamine or polyamine component embodies a broad class
33 of amines having from 1 to about 12 amine nitrogen atoms and
34

-9-

01 from 1 to 40 carbon atoms with a carbon to nitrogen ratio
02 between about 1:1 and 10:1. Generally, the monoamine will
03 contain from 1 to about 40 carbon atoms and the polyamine
04 will contain from 2 to about 12 amine nitrogen atoms and
05 from 2 to about 40 carbon atoms. In most instances, the
06 amine component is not a pure single product, but rather a
07 mixture of compounds having a major quantity of the
08 designated amine. For the more complicated polyamines, the
09 compositions will be a mixture of amines having as the major
10 product the compound indicated and having minor amounts of
11 analogous compounds. Suitable monoamines and polyamines are
12 described more fully below.

13 When the amine component is a polyamine, it will preferably
14 be a polyalkylene polyamine, including alkylenediamine.
15 Preferably, the alkylene group will contain from 2 to
16 6 carbon atoms, more preferably from 2 to 3 carbon atoms.
17 Examples of such polyamines include ethylene diamine,
18 diethylene triamine, triethylene tetramine and tetraethylene
19 pentamine. Preferred polyamines are ethylene diamine and
20 diethylene triamine.

22 Particularly preferred branched-chain hydrocarbyl amines
23 include polyisobutetyl ethylene diamine and polyisobutyl
24 amine, wherein the polyisobutyl group is substantially
25 saturated and the amine moiety is derived from ammonia.

27 The aliphatic hydrocarbyl amines employed in the fuel
28 additive composition of the invention are prepared by
29 conventional procedures known in the art. Such aliphatic
30 hydrocarbyl amines and their preparations are described in
31 detail in U.S. Patent Nos. 3,438,757; 3,565,804; 3,574,576;
32 3,848,056; 3,960,515; and 4,832,702, the disclosures of
33 which are incorporated herein by reference.

-10-

01 Typically, the hydrocarbyl-substituted amines employed in
02 this invention are prepared by reacting a hydrocarbyl
03 halide, such as a hydrocarbyl chloride, with ammonia or a
04 primary or secondary amine to produce the hydrocarbyl-
05 substituted amine.

06
07 As noted above, the amine component of the presently
08 employed hydrocarbyl-substituted amine is derived from a
09 nitrogen-containing compound selected from ammonia, a
10 monoamine having from 1 to 40 carbon atoms, and a polyamine
11 having from 2 to about 12 amine nitrogen atoms and from 2 to
12 about 40 carbon atoms. The nitrogen-containing compound is
13 reacted with a hydrocarbyl halide to produce the
14 hydrocarbyl-substituted amine fuel additive finding use
15 within the scope of the present invention. The amine
16 component provides a hydrocarbyl amine reaction product
17 with, on average, at least about one basic nitrogen atom per
18 product molecule, i.e., a nitrogen atom titratable by a
19 strong acid.

20
21 Preferably, the amine component is derived from a polyamine
22 having from 2 to about 12 amine nitrogen atoms and from 2 to
23 about 40 carbon atoms. The polyamine preferably has a
24 carbon-to-nitrogen ratio of from about 1:1 to 10:1.

25
26 The polyamine may be substituted with substituents selected
27 from (A) hydrogen, (B) hydrocarbyl groups of from 1 to about
28 10 carbon atoms, (C) acyl groups of from 2 to about 10
29 carbon atoms, and (D) monoketo, monohydroxy, mononitro,
30 monocyno, lower alkyl and lower alkoxy derivatives of (B)
31 and (C). "Lower", as used in terms like lower alkyl or
32 lower alkoxy, means a group containing from 1 to about
33 6 carbon atoms. At least one of the substituents on one of
34 the basic nitrogen atoms of the polyamine is hydrogen, e.g.,

WO 95/29973

-11-

01 at least one of the basic nitrogen atoms of the polyamine is
02 a primary or secondary amino nitrogen.

03
04 Hydrocarbyl, as used in describing the polyamine moiety on
05 the aliphatic amine employed in this invention, denotes an
06 organic radical composed of carbon and hydrogen which may be
07 aliphatic, alicyclic, aromatic or combinations thereof,
08 e.g., aralkyl. Preferably, the hydrocarbyl group will be
09 relatively free of aliphatic unsaturation, i.e., ethylenic
10 and acetylenic, particularly acetylenic unsaturation. The
11 substituted polyamines of the present invention are
12 generally, but not necessarily, N-substituted polyamines.
13 Exemplary hydrocarbyl groups and substituted hydrocarbyl
14 groups include alkyls such as methyl, ethyl, propyl, butyl,
15 isobutyl, pentyl, hexyl, octyl, etc., alkenyls such as
16 propenyl, isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls,
17 such as 2-hydroxyethyl, 3-hydroxypropyl, hydroxy-isopropyl,
18 4-hydroxybutyl, etc., ketoalkyls, such as 2-ketopropyl,
19 6-ketoctyl, etc., alkoxy and lower alenoxy alkyls, such as
20 ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl,
21 diethyleneoxymethyl, triethyleneoxyethyl,
22 tetraethyleneoxyethyl, diethyleneoxyhexyl, etc. The
23 aforementioned acyl groups (C) are such as propionyl,
24 acetyl, etc. The more preferred substituents are hydrogen,
25 C₁-C₆ alkyls and C₁-C₆ hydroxyalkyls.

26
27 In a substituted polyamine, the substituents are found at
28 any atom capable of receiving them. The substituted atoms,
29 e.g., substituted nitrogen atoms, are generally
30 geometrically unequivalent, and consequently the substituted
31 amines finding use in the present invention can be mixtures
32 of mono- and poly-substituted polyamines with substituent
33 groups situated at equivalent and/or unequivalent atoms.

34

-12-

01 The more preferred polyamine finding use within the scope of
02 the present invention is a polyalkylene polyamine, including
03 alkylene diamine, and including substituted polyamines,
04 e.g., alkyl and hydroxyalkyl-substituted polyalkylene
05 polyamine. Preferably, the alkylene group contains from 2
06 to 6 carbon atoms, there being preferably from 2 to 3 carbon
07 atoms between the nitrogen atoms. Such groups are
08 exemplified by ethylene, 1,2-propylene, 2,2-dimethyl-
09 propylene, trimethylene, 1,3,2-hydroxypropylene, etc.
10 Examples of such polyamines include ethylene diamine,
11 diethylene triamine, di(trimethylene) triamine, dipropylene
12 triamine, triethylene tetraamine, tripropylene tetraamine,
13 tetraethylene pentamine, and pentaethylene hexamine. Such
14 amines encompass isomers such as branched-chain polyamines
15 and previously-mentioned substituted polyamines, including
16 hydroxy- and hydrocarbyl-substituted polyamines. Among the
17 polyalkylene polyamines, those containing 2-12 amino
18 nitrogen atoms and 2-24 carbon atoms are especially
19 preferred, and the C₂-C₃ alkylene polyamines are most
20 preferred, that is, ethylene diamine, polyethylene
21 polyamine, propylene diamine and polypropylene polyamine,
22 and in particular, the lower polyalkylene polyamines, e.g.,
23 ethylene diamine, dipropylene triamine, etc. Particularly
24 preferred polyalkylene polyamines are ethylene diamine and
25 diethylene triamine.

26
27 The amine component of the presently employed aliphatic
28 amine fuel additive also may be derived from heterocyclic
29 polyamines, heterocyclic substituted amines and substituted
30 heterocyclic compounds, wherein the heterocycle comprises
31 one or more 5-6 membered rings containing oxygen and/or
32 nitrogen. Such heterocyclic rings may be saturated or
33 unsaturated and substituted with groups selected from the
34

WO 95/29973

-13-

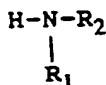
01 aforementioned (A), (B), (C) and (D). The heterocyclic
02 compounds are exemplified by piperazines, such as
03 2-methylpiperazine, N-(2-hydroxyethyl)-piperazine,
04 1,2-bis-(N-piperazinyl)ethane and
05 N,N'-bis(N-piperazinyl)piperazine, 2-methylimidazoline,
06 3-aminopiperidine, 3-aminopyridine, N-(3-aminopropyl)-
07 morpholine, etc. Among the heterocyclic compounds, the
08 piperazines are preferred.

09 Typical polyamines that can be used to form the aliphatic
10 amine additives employed in this invention by reaction with
11 a hydrocarbyl halide include the following: ethylene
12 diamine, 1,2-propylene diamine, 1,3-propylene diamine,
13 diethylene triamine, triethylene tetramine, hexamethylene
14 diamine, tetraethylene pentamine, dimethylaminopropylene
15 diamine, N-(beta-aminoethyl)piperazine, N-(beta-
16 aminoethyl)piperidine, 3-amino-N-ethylpiperidine, N-(beta-
17 aminoethyl) morpholine, N,N'-di(beta-aminoethyl)piperazine,
18 N,N'-di(beta-aminoethyl)imidazolidone-2, N-(beta-cyanoethyl)
19 ethane-1,2-diamine, 1-amino-3,6,9-triazaoctadecane,
20 1-amino-3,6-diaza-9-oxadecane, N-(beta-aminoethyl)
21 diethanolamine, N'acetyl methyl-N-(beta-aminoethyl)
22 ethane-1,2-diamine, N-acetonyl-1,2-propanediamine,
23 N-(beta-nitroethyl)-1,3-propane diamine,
24 1,3-dimethyl-5(beta-aminoethyl)hexahydrotriazine, N-(beta-
25 aminoethyl)-hexahydrotriazine, 5-(beta-aminoethyl)-
26 1,3,5-dioxazine, 2-(2-aminoethylamino)ethanol, and
27 2-[2-(2-aminoethylamino) ethylamino]ethanol.

28
29 Alternatively, the amine component of the presently employed
30 aliphatic hydrocarbyl-substituted amine may be derived from
31 an amine having the formula:

32
33
34

-14-



01
02
03
04 wherein R_1 and R_2 are independently selected from the group
05 consisting of hydrogen and hydrocarbyl of 1 to about
06 20 carbon atoms and, when taken together, R_1 and R_2 may form
07 one or more 5- or 6-membered rings containing up to about
08 20 carbon atoms. Preferably, R_1 is hydrogen and R_2 is a
09 hydrocarbyl group having 1 to about 10 carbon atoms. More
10 preferably, R_1 and R_2 are hydrogen. The hydrocarbyl groups
11 may be straight-chain or branched and may be aliphatic,
12 alicyclic, aromatic or combinations thereof. The
13 hydrocarbyl groups may also contain one or more oxygen
14 atoms.
15

16 An amine of the above formula is defined as a "secondary
17 amine" when both R_1 and R_2 are hydrocarbyl. When R_1 is
18 hydrogen and R_2 is hydrocarbyl, the amine is defined as a
19 "primary amine"; and when both R_1 and R_2 are hydrogen, the
20 amine is ammonia.
21

22 Primary amines useful in preparing the aliphatic
23 hydrocarbyl-substituted amine fuel additives of the present
24 invention contain 1 nitrogen atom and 1 to about 20 carbon
25 atoms, preferably 1 to 10 carbon atoms. The primary amine
26 may also contain one or more oxygen atoms.
27

28 Preferably, the hydrocarbyl group of the primary amine is
29 methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl,
30 2-hydroxyethyl or 2-methoxyethyl. More preferably, the
31 hydrocarbyl group is methyl, ethyl or propyl.
32
33
34

WO 95/29973

-15-

- 01 Typical primary amines are exemplified by N-methylamine,
02 N-ethylamine, N-n-propylamine, N-isopropylamine,
03 N-n-butylamine, N-isobutylamine, N-sec-butylamine,
04 N-tert-butylamine, N-n-pentylamine, N-cyclopentylamine,
05 N-n-hexylamine, N-cyclohexylamine, N-octylamine,
06 N-decylamine, N-dodecylamine, N-octadecylamine,
07 N-benzylamine, N-(2-phenylethyl)amine, 2-aminoethanol,
08 3-amino-1-propanol, 2-(2-aminoethoxy)ethanol,
09 N-(2-methoxyethyl)amine, N-(2-ethoxyethyl)amine, and the
10 like. Preferred primary amines are N-methylamine,
11 N-ethylamine and N-n-propylamine.
- 12 The amine component of the presently employed aliphatic
13 hydrocarbyl-substituted amine fuel additive may also be
14 derived from a secondary amine. The hydrocarbyl groups of
15 the secondary amine may be the same or different and will
16 generally contain 1 to about 20 carbon atoms, preferably 1
17 to about 10 carbon atoms. One or both of the hydrocarbyl
18 groups may also contain one or more oxygen atoms.
19
- 20 Preferably, the hydrocarbyl groups of the secondary amine
21 are independently selected from the group consisting of
22 methyl, ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl
23 and 2-methoxyethyl. More preferably, the hydrocarbyl groups
24 are methyl, ethyl or propyl.
- 25
- 26 Typical secondary amines which may be used in this invention
27 include N,N-dimethylamine, N,N-diethylamine, N,N-di-n-
28 propylamine, N,N-diisopropylamine, N,N-di-n-butylamine,
29 N,N-di-sec-butylamine, N,N-di-n-pentylamine, N,N-di-n-
30 hexylamine, N,N-dicyclohexylamine, N,N-dioctylamine,
31 N-ethyl-N-methylamine, N-methyl-N-n-propylamine, N-n-butyl-
32 N-methylamine, N-methyl-N-octylamine, N-ethyl-N-
33 isopropylamine, N-ethyl-N-octylamine,
34

WO 95/29973

-16-

01 N,N-di(2-hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine,
02 N,N-di(ethoxyethyl)amine, N,N-di(propoxymethyl)amine, and the
03 like. Preferred secondary amines are N,N-dimethylamine,
04 N,N-diethylamine and N,N-di-n-propylamine.

05 Cyclic secondary amines may also be employed to form the
06 aliphatic amine additives of this invention. In such cyclic
07 compounds, R₁ and R₂ of the formula hereinabove, when taken
08 together, form one or more 5- or 6-membered rings containing
09 up to about 20 carbon atoms. The ring containing the amine
10 nitrogen atom is generally saturated, but may be fused to
11 one or more saturated or unsaturated rings. The rings may
12 be substituted with hydrocarbyl groups of from 1 to about
13 10 carbon atoms and may contain one or more oxygen atoms.
14

15 Suitable cyclic secondary amines include piperidine,
16 4-methylpiperidine, pyrrolidine, morpholine,
17 2,6-dimethylmorpholine, and the like.

18
19 In many instances, the amine component is not a single
20 compound but a mixture in which one or several compounds
21 predominate with the average composition indicated. For
22 example, tetraethylene pentamine prepared by the
23 polymerization of aziridine or the reaction of
24 dichloroethylene and ammonia will have both lower and higher
25 amine members, e.g., triethylene tetraamine, substituted
26 piperazines and pentaethylene hexamine, but the composition
27 will be mainly tetraethylene pentamine and the empirical
28 formula of the total amine composition will closely
29 approximate that of tetraethylene pentamine. Finally, in
30 preparing the compounds of this invention using a polyamine,
31 where the various nitrogen atoms of the polyamine are not
32 geometrically equivalent, several substitutional isomers are
33
34

WO 95/29973

-17-

01 possible and are encompassed within the final product.
02 Methods of preparation of amines and their reactions are
03 detailed in Sidgewick's "The Organic Chemistry of Nitrogen",
04 Clarendon Press, Oxford, 1966; Noller's "Chemistry of
05 Organic Compounds", Saunders, Philadelphia, 2nd Ed., 1957;
06 and Kirk-Othmer's "Encyclopedia of Chemical Technology",
07 2nd Ed., especially Volume 2, pp. 99-116.

08 Preferred aliphatic hydrocarbyl-substituted amines suitable
09 for use in the present invention are hydrocarbyl-substituted
10 polyalkylene polyamines having the formula:
11



14
15 wherein R_3 is a hydrocarbyl group having a number average
16 molecular weight of about 700 to 3,000; R_4 is alkylene of
17 from 2 to 6 carbon atoms; and n is an integer of from 0 to
18 about 10.

19
20 Preferably, R_3 is a hydrocarbyl group having a number
21 average molecular weight of about 750 to 2,200, more
22 preferably, from about 900 to 1,500. Preferably, R_4 is
23 alkylene of from 2 to 3 carbon atoms and n is preferably an
24 integer of from 1 to 6.
25

26 B. The Polyolefin Polymer
27

28 The polyolefin polymer component of the present fuel
29 additive composition is a polyolefin polymer of a C_2 to C_6
30 monoolefin, wherein the polyolefin polymer has a number
31 average molecular weight of about 350 to 3,000. The
32 polyolefin polymer may be a homopolymer or a copolymer.
33

34

-18-

01 Block copolymers are also suitable for use in this
02 invention.

03
04 In general, the polyolefin polymer will have a number
05 average molecular weight of about 350 to 3,000, preferably
06 about 350 to 1,500, and more preferably from about 350 to
07 500. Particularly preferred polyolefin polymers will have a
08 number average molecular weight of about 375 to 450.

09
10 The polyolefin polymers employed in the present invention
11 are generally polyolefins which are polymers or copolymers
12 of mono-olefins, particularly 1-mono-olefins, such as
13 ethylene, propylene, butylene, and the like. Preferably,
14 the mono-olefin employed will have 2 to about 4 carbon
15 atoms, and more preferably, about 3 to 4 carbon atoms. More
16 preferred mono-olefins include propylene and butylene,
17 particularly isobutylene. Polyolefins prepared from such
18 mono-olefins include polypropylene and polybutene,
19 especially polyisobutene.

20
21 The polyisobutenes which are suitable for use in the present
22 invention include polyisobutenes which comprise at least
23 about 20% of the more reactive methylvinylidene isomer,
24 preferably at least 50% and more preferably at least 70%.
25 Suitable polyisobutenes include those prepared using BF_3
26 catalysts. The preparation of such polyisobutenes in which
27 the methylvinylidene isomer comprises a high percentage of
28 the total composition is described in U.S. Patent
29 Nos. 4,152,499 and 4,605,808.

30
31 Examples of suitable polyisobutenes having a high
32 alkylvinylidene content include Ultravis 30, a polyisobutene
33 having a number average molecular weight of about 1300 and a
34

WO 95/29973

-19-

01 methylvinylidene content of about 74%, and Ultravis 10, a
02 950 molecular weight polyisobutene having a methylvinylidene
03 content of about 76%, both available from British Petroleum.

04 Preferred polyisobutenes include those having a number
05 average molecular weight of about 375 to 450, such as
06 Parapol 450, a polyisobutene having a number average
07 molecular weight of about 420, available from Exxon Chemical
08 Company.

10

11 C. The Aromatic Ester

12

13 The aromatic ester component of the present fuel additive
14 composition is an aromatic di- or tri-carboxylic acid ester
15 having the formula:



WO 95/29973

-20-

- 01 tri-carboxylic acid with a straight or branched chain
02 aliphatic alcohol having 4 to 20 carbon atoms.
03 Suitable aromatic di- or tri-carboxylic acid esters finding
04 use in the present invention include phthalic acid esters,
05 isophthalic acid esters, terephthalic acid esters,
06 trimellitic acid esters, and the like. Preferred aromatic
07 esters are phthalate, isophthalate and terephthalate esters.
08 More preferably, the aromatic ester is a phthalate ester. A
09 particularly preferred aromatic ester is di-isodecyl
10 phthalate.
11
12 A preferred fuel additive composition within the scope of
13 the present invention is one wherein component (a) is a
14 polyisobut enyl amine, wherein the amine moiety is derived
15 from ethylene diamine or diethylene triamine, component (b)
16 is polyisobutene, and component (c) is a phthalate ester.
17

18 Fuel Compositions
19

- 20 The fuel additive composition of the present invention will
21 generally be employed in a hydrocarbon distillate fuel
22 boiling in the gasoline or diesel range. The proper
23 concentration of this additive composition necessary in
24 order to achieve the desired detergency and dispersancy
25 varies depending upon the type of fuel employed, the
26 presence of other detergents, dispersants and other
27 additives, etc. Generally, however, from 150 to 7500 weight
28 ppm, preferably from 300 to 2500 ppm, of the present
29 additive composition per part of base fuel is needed to
30 achieve the best results.
31
32 In terms of individual components, fuel compositions
33 containing the additive compositions of the invention will
34

WO 95/29973

-21-

01 generally contain about 50 to 500 ppm by weight of the
02 aliphatic amine, about 50 to 1,000 ppm by weight of the
03 polyolefin, and about 50 to 1,000 ppm by weight of the
04 aromatic ester. The ratio of aliphatic amine to polyolefin
05 to aromatic ester (amine:polyolefin:ester) will generally be
06 in the range of about 1 : 0.5 to 10 : 0.5 to 10, preferably
07 about 1 : 1 to 5 : 1 to 5, and more preferably about 1:1:1.

08
09 The deposit control fuel additive composition may be
10 formulated as a concentrate, using an inert stable
11 oleophilic (i.e., dissolves in gasoline) organic solvent
12 boiling in the range of about 150°F to 400°F (about 65°C to
13 205°C). Preferably, an aliphatic or an aromatic hydrocarbon
14 solvent is used, such as benzene, toluene, xylene or
15 higher-boiling aromatics or aromatic thinners. Aliphatic
16 alcohols of about 3 to 8 carbon atoms, such as isopropanol,
17 isobutylcarbinol, n-butanol and the like, in combination
18 with hydrocarbon solvents are also suitable for use with the
19 detergent-dispersant additive. In the concentrate, the
20 amount of the present additive composition will be
21 ordinarily at least 10% by weight and generally not exceed
22 90% by weight, preferably 40 to 85 weight percent and most
23 preferably from 50 to 80 weight percent.

24
25 In gasoline fuels, other fuel additives may be employed with
26 the additives of the present invention, including, for
27 example, oxygenates, such as t-butyl methyl ether, antiknock
28 agents, such as methylcyclopentadienyl manganese
29 tricarbonyl, and other dispersants/detergents, such as
30 various hydrocarbyl amines, hydrocarbyl poly(oxyalkylene)
31 amines, or succinimides. Also included may be lead
32 scavengers, such as aryl halides, e.g., dichlorobenzene, or
33 alkyl halides, e.g., ethylene dibromide. Additionally,
34 antioxidants, metal deactivators, pour point depressants,

-22-

01 corrosion inhibitors and demulsifiers may be present. The
02 gasoline fuels may also contain amounts of other fuels such
03 as, for example, methanol.

04 Additional fuel additives which may be present include
05 fuel injector inhibitors, low molecular weight fuel
06 injector detergents, and carburetor detergents, such as a
07 low molecular weight hydrocarbyl amine, including
08 polyamines, having a molecular weight below 700, such as
09 oleyl amine or a low molecular weight polyisobutylene
10 ethylene diamine, for example, where the polyisobutylene
11 group has a number average molecular weight of about 420.
12

13 In diesel fuels, other well-known additives can be employed,
14 such as pour point depressants, flow improverse, cetane
15 improvers, and the like. The diesel fuels can also include
16 other fuels such as, for example, methanol.
17

18 A fuel-soluble, nonvolatile carrier fluid or oil may also be
19 used with the fuel additive composition of this invention.
20 The carrier fluid is a chemically inert hydrocarbon-soluble
21 liquid vehicle which substantially increases the nonvolatile
22 residue (NVR), or solvent-free liquid fraction of the fuel
23 additive composition while not overwhelmingly contributing
24 to octane requirement increase. The carrier fluid may be a
25 natural or synthetic oil, such as mineral oil or refined
26 petroleum oils.
27

28 These carrier fluids are believed to act as a carrier for
29 the fuel additives of the present invention and to assist in
30 removing and retarding deposits. The carrier fluid may also
31 exhibit synergistic deposit control properties when used in
32 combination with a fuel additive composition of this
33 invention.
34

WO 95/29973

-23-

01 The carrier fluids are typically employed in amounts ranging
02 from about 50 to about 2000 ppm by weight of the hydrocarbon
03 fuel, preferably from 100 to 800 ppm of the fuel.
04 Preferably, the ratio of carrier fluid to deposit control
05 additive will range from about 0.5:1 to about 10:1, more
06 preferably from 1:1 to 4:1.

07
08 When employed in a fuel concentrate, carrier fluids will
09 generally be present in amounts ranging from about 10 to
10 about 60 weight percent, preferably from 20 to 40 weight
11 percent.

12
13 The following examples are presented to illustrate specific
14 embodiments of this invention and are not to be construed in
15 any way as limiting the scope of the invention.

16 EXAMPLES

17
18 Example A1

19
20 An engine test was carried out using commercial regular
21 unleaded gasoline to measure deposits on intake valves and
22 combustion chambers using this fuel. The test engine was a
23 2.3 liter, Port Fuel Injected (PFI), dual spark plug,
24 four-cylinder engine manufactured by Ford Motor Company.
25 Major dimensions are set forth in Table 1.

26
27
28
29
30
31
32
33
34

-24-

Table 1
Engine Dimensions

Bore	96 mm
Stroke	79.3 mm
Displacement	2.3 liter
Compression Ratio	10.3 : 1

The test engine was operated for 100 hours (24 hours a day) on a prescribed load and speed schedule specified by the Coordinating Research Council as a standard condition for Intake Valve Deposit testing. The cycle for engine operation is set forth in Table 2.

Table 2
Engine Operating Cycle

Step	Mode	Time in Mode [minute] ¹	Engine Speed [RPM]	Manifold Pressure [mm Hg Abs.]
1	Idle	4.5	2000	223
2	Load	8.5	2800	522

¹Each step includes a 30-second transition ramp.

At the end of each test run, the intake valves were removed, washed with hexane, and weighed. The previously determined weights of the clean valves were subtracted from the weights of the valves at the end of the run. The difference between the two weights is the weight of the intake valve deposit (IVD). Also, for each cylinder, the piston top and the mating surface of the cylinder head were scraped and the

-25-

01 deposit removed was weighed as the measure of the combustion
02 chamber deposit (CCD). The results are set forth in Table 3
03 below.

04

Example A2

05

06 A sample fuel composition A2 was prepared by adding:
07

08

09 (1) 125 ppm by weight di-isodecyl phthalate ester, and

10

11 (2) 125 ppma (parts per million actives) by weight of a
12 hydrocarbyl amine having a 1300 MW polyisobutenyl
13 moiety and an ethylene diamine moiety

14

15 to the gasoline of Example A1.

16

17 The same experiment as in Example A1 was carried out using
18 this fuel composition, and the results are shown in Table 3
19 below.

20

Example A3

21

22 A sample fuel composition A3 was prepared by adding:
23

24

25 (1) 125 ppm by weight of 420 number average molecular
26 weight polyisobutene, and

27

28 (2) 125 ppma by weight of a hydrocarbyl amine having a
29 1300 MW polyisobutenyl moiety and an ethylene diamine
30 moiety

31

32 to the gasoline of Example A1.

33

34

-26-

01 The same experiment as in Example A1 was carried out using
02 this fuel composition, and the results are shown in Table 3
03 below.

04

05 Example A4

06

07 A sample fuel composition A4 was prepared by adding:

08

09 (1) 125 ppm by weight of 420 number average molecular
10 weight polyisobutene; and

11

12 (2) 125 ppm by weight di-isodecyl phthalate ester, and

13

14 (3) 125 ppma by weight of a hydrocarbyl amine having a
15 1300 MW polyisobutetyl moiety and an ethylene diamine
16 moiety

17

18 to the gasoline of Example A1.

19

20 The same experiment as in Example A1 was carried out using
21 this fuel composition, and the results are shown in Table 3
22 below.

23

24 Table 3
25 Ford 2.3 Liter Engine Test Results

26

27 <u>Test Fuel Detergent Package</u>	28 <u>Average Weight per Cylinder</u>	
	29 IVD (mg)	30 CCD (mg)
31 Base Fuel A1	419	949
32 Fuel Composition A2	715	1340
33 Fuel Composition A3	580	1201
34 Fuel Composition A4	577	1485

-27-

01 The results in Table 3 show that the fuel additive
02 composition of the present invention (Example A4) exhibits
03 very good intake valve deposit control performance,
04 equivalent to or better than the two-component additive
05 compositions of Examples A2 and A3, while maintaining a low
06 level of combustion chamber deposits.

07

Example B1

08

09

10 An engine test was carried out using Phillips-J gasoline, an
11 industry testing fuel, to evaluate its tendency to cause
12 intake valve stickiness. The test engine was a 2-cylinder,
13 4-stroke, overhead-cam, liquid-cooled Honda generator model
14 ES6500. Major specifications for the Honda generator are
15 set forth in Table 4.

16

17

18

Table 4
Engine Specifications

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

Bore	56 mm
Stroke	68 mm
Displacement	0.369 liter
Maximum Horsepower	12.2 HP @ 3600 rpm

The test procedure includes 80 hours of continuous operation
on the test fuel. The test cycle consists of two 2-hour
stages. The stage conditions are set forth in Table 5.

-28-

Table 5
Engine Operating Cycle

Stage	Time in stage [hour]	Engine Speed [RPM]	Generator Load [watt]
1	2.0	3000	1500
2	2.0	3000	2500

¹Each step includes a short transition ramp.

During the test, the generator speed was maintained by automatic control of the engine throttle. A bank of incandescent bulbs with various electrical load ratings were used to induce the load on the generator.

At the end of each test, the engine was disassembled and the cylinder head, with valve springs and seals removed, and with the valves open, was stored in a freezer at 5°F overnight. The stickiness of the valves were determined by using a load cell to measure the force required to close each valve at an approximate speed of 1.22 mm/sec (3 in/min). The magnitude of this force has been found to correlate with the tendency of the test fuel to cause sticking valves in vehicles. The results are set forth in Table 6 below.

Example B2

28 A sample fuel composition B2 was prepared by adding:
29

WO 95/29973

-29-

01 (2) 160 ppma by weight of a hydrocarbyl amine having a
02 1300 MW polyisobutetyl moiety and an ethylene diamine
03 moiety
04
05 to the gasoline of Example B1.

06
07 The same experiment as in Example B1 was carried out using
08 this fuel composition, and the results are shown in Table 6
09 below.

10
11 Example B3

12
13 A sample fuel composition B3 was prepared by adding:

14
15 (1) 160 ppm by weight of 420 number average molecular
16 weight polyisobutene, and

17
18 (2) 160 ppma by weight of a hydrocarbyl amine having a
19 1300 MW polyisobutetyl moiety and an ethylene diamine
20 moiety

21
22 to the gasoline of Example B1.

23
24 The same experiment as in Example B1 was carried out using
25 this fuel composition, and the results are shown in Table 6
26 below.

27
28 Example B4

29
30 A sample fuel composition B4 was prepared by adding:

31
32 (1) 160 ppm by weight of 420 number average molecular
33 weight polyisobutene; and

34

-30-

01 (2) 160 ppm by weight di-isodecyl phthalate ester, and
02
03 (3) 160 ppma by weight of a hydrocarbyl amine having a
04 1300 MW polyisobutenyl moiety and an ethylene diamine
05 moiety
06
07 to the gasoline of Example B1.

08
09 The same experiment as in Example B1 was carried out using
10 this fuel composition, and the results are shown in Table 6
11 below.

12

13 Table 6
14 Honda Generator Engine Test Results

15

Test Fuel Detergent Package	Force Required To Close Valves (newton)	
	Valve #1	Valve #2
Fuel Composition B2	51.6	88.9
Fuel Composition B3	71.1	84.5
Fuel Composition B4	1.3	29.8

23

24 The data in Table 6 illustrates the significant reduction in
25 stickiness of the valves provided by the fuel composition of
26 Example B4 as compared to the fuel compositions of
27 Examples B2 and B3.
28

29

30 Example C

31

32 Fuel additive compositions of the present invention are also
33 prepared which contain:

34

WO 95/29973

-31-

- 01 (1) 125 ppm by weight of 420 number average molecular
02 weight polyisobutene;
- 03
- 04 (2) 125 ppm by weight di-isodecyl phthalate ester;
- 05
- 06 (3) 125 ppma by weight of a hydrocarbyl amine having a
07 1300 MW polyisobutenyl moiety and an ethylene diamine
08 moiety;
- 09
- 10 and at least one of the following components:
- 11
- 12 (4) 125-250 ppm of a mineral oil carrier fluid; and/or
- 13
- 14 (5) 10-50 ppm, preferably 20 ppm, of a low molecular weight
15 hydrocarbyl amine carburetor or injector detergent,
16 such as oleyl amine or polyisobutenyl (420 MW) ethylene
17 diamine.
- 18
- 19
- 20
- 21
- 22
- 23
- 24
- 25
- 26
- 27
- 28
- 29
- 30
- 31
- 32
- 33
- 34

-32-

01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

04

05 (a) a fuel-soluble aliphatic hydrocarbyl-substituted
06 amine having at least one basic nitrogen atom
07 wherein the hydrocarbyl group has a number average
08 molecular weight of about 700 to 3,000;

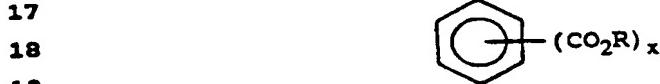
09

10 (b) a polyolefin polymer of a C₂ to C₆ monoolefin,
11 wherein the polymer has a number average molecular
12 weight of about 350 to 3,000; and

13

14 (c) an aromatic di- or tri-carboxylic acid ester of
15 the formula:

16



17

18 where R is an alkyl group of 4 to 20 carbon
19 atoms, and x is 2 or 3.

20

21 2. The fuel additive composition according to Claim 1,
22 wherein the hydrocarbyl substituent on the aliphatic
23 amine of component (a) has a number average molecular
24 weight of about 750 to 2,200.

25

26 3. The fuel additive composition according to Claim 2,
27 wherein the hydrocarbyl substituent on the aliphatic
28 amine of component (a) has a number average molecular
29 weight of about 900 to 1,500.

30

31

32

33

34

-33-

- 01 4. The fuel additive composition according to Claim 1,
02 wherein the aliphatic amine of component (a) is a
03 branched chain hydrocarbyl-substituted amine.
- 04
- 05 5. The fuel additive composition according to Claim 4,
06 wherein the aliphatic amine of component (a) is a
07 polyisobut enyl amine.
- 08
- 09 6. The fuel additive composition according to Claim 4,
10 wherein the amine moiety of the aliphatic amine is
11 derived from a polyamine having from 2 to 12 amine
12 nitrogen atoms and from 2 to 40 carbon atoms.
- 13
- 14 7. The fuel additive composition according to Claim 6,
15 wherein the polyamine is a polyalkylene polyamine
16 having 2 to 12 amine nitrogen atoms and 2 to 24 carbon
17 atoms.
- 18
- 19 8. The fuel additive composition according to Claim 7,
20 wherein the polyalkylene polyamine is selected from the
21 group consisting of ethylene diamine, diethylene
22 triamine, triethylene tetramine and tetraethylene
23 pentamine.
- 24
- 25 9. The fuel additive composition according to Claim 8,
26 wherein the polyalkylene polyamine is ethylene diamine
27 or diethylene triamine.
- 28
- 29 10. The fuel additive composition according to Claim 9,
30 wherein the aliphatic amine of component (a) is a
31 polyisobut enyl ethylene diamine.

32

33

34

WO 95/29973

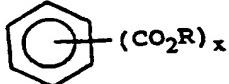
-34-

- 01 11. The fuel additive composition according to Claim 1,
02 wherein the polyolefin polymer of component (b) is a
03 polymer of a C₂ to C₄ monoolefin.
- 04 12. The fuel additive composition according to Claim 11,
05 wherein the polyolefin polymer of component (b) is
06 polypropylene or polybutene.
- 07 13. The fuel additive composition according to Claim 12,
08 wherein the polyolefin polymer of component (b) is
09 polyisobutene.
- 10 14. The fuel additive composition according to Claim 1,
11 wherein the polyolefin polymer of component (b) has a
12 number average molecular weight of about 350 to 1500.
- 13 15. The fuel additive composition according to Claim 14,
14 wherein the polyolefin polymer of component (b) has a
15 number average molecular weight of about 350 to 500.
- 16 16. The fuel additive composition according to Claim 1,
17 wherein the aromatic ester of component (c) is a
18 phthalate, isophthalate or terephthalate ester.
- 19 17. The fuel additive composition according to Claim 16,
20 wherein the aromatic ester of component (c) is a
21 phthalate ester.
- 22 18. The fuel additive composition according to Claim 1,
23 wherein the R group on the aromatic ester of component
24 (c) is alkyl of 8 to 13 carbon atoms.

WO 95/29973

-35-

- 01 19. The fuel additive composition according to Claim 1,
02 wherein component (a) is a polyisobut enyl amine,
03 wherein the amine moiety is derived from ethylene
04 diamine or diethylene triamine, component (b) is
05 polyisobutene, and component (c) is a phthalate ester.
- 06 20. A fuel composition comprising a major amount of
07 hydrocarbons boiling in the gasoline or diesel range
08 and an effective detergent amount of an additive
09 composition comprising:
10
- 11 (a) a fuel-soluble aliphatic hydrocarbyl-substituted
12 amine having at least one basic nitrogen atom
13 wherein the hydrocarbyl group has a number average
14 molecular weight of about 700 to 3,000;
- 15 (b) a polyolefin polymer of a C₂ to C₆ monoolefin,
16 wherein the polymer has a number average molecular
17 weight of about 350 to 3,000; and
18
- 19 (c) an aromatic di- or tri-carboxylic acid ester of
20 the formula:
21



22
23
24
25
26
27
28
29
30
31
32
33
34

wherein R is an alkyl group of 4 to 20 carbon atoms, and x is 2 or 3.

-36-

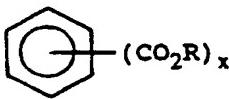
- 01 21. The fuel composition according to Claim 20, wherein the hydrocarbyl substituent on the aliphatic amine of component (a) has a number average molecular weight of about 750 to 2,200.
- 05 22. The fuel composition according to Claim 21, wherein the hydrocarbyl substituent on the aliphatic amine of component (a) has a number average molecular weight of about 900 to 1,500.
- 10 23. The fuel composition according to Claim 20, wherein the aliphatic amine of component (a) is a branched chain hydrocarbyl-substituted amine.
- 14 24. The fuel composition according to Claim 23, wherein the aliphatic amine of component (a) is a polyisobutenyl amine.
- 18 25. The fuel composition according to Claim 23, wherein the amine moiety of the aliphatic amine is derived from a polyamine having from 2 to 12 amine nitrogen atoms and from 2 to 40 carbon atoms.
- 23 26. The fuel composition according to Claim 25, wherein the polyamine is a polyalkylene polyamine having 2 to 12 amine nitrogen atoms and 2 to 24 carbon atoms.
- 27 27. The fuel composition according to Claim 26, wherein the polyalkylene polyamine is selected from the group consisting of ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentamine.
- 32
- 33
- 34

WO 95/29973

-37-

- 01 28. The fuel composition according to Claim 27, wherein the
02 polyalkylene polyamine is ethylene diamine or
03 diethylene triamine.
- 04 29. The fuel composition according to Claim 28, wherein the
05 aliphatic amine of component (a) is a polyisobut enyl
06 ethylene diamine.
- 07
- 08 30. The fuel composition according to Claim 20, wherein the
09 polyolefin polymer of component (b) is a polymer of a
10 C₂ to C₄ monoolefin.
- 11
- 12 31. The fuel composition according to Claim 30, wherein the
13 polyolefin polymer of component (b) is polypropylene or
14 polybutene.
- 15
- 16 32. The fuel composition according to Claim 31, wherein the
17 polyolefin polymer of component (b) is polyisobutene.
- 18
- 19 33. The fuel composition according to Claim 20, wherein the
20 polyolefin polymer of component (b) has a number
21 average molecular weight of about 350 to 1500.
- 22
- 23 34. The fuel composition according to Claim 33, wherein the
24 polyolefin polymer of component (b) has a number
25 average molecular weight of about 350 to 500.
- 26
- 27 35. The fuel composition according to Claim 20, wherein the
28 aromatic ester of component (c) is a phthalate,
29 isophthalate or terephthalate ester.
- 30
- 31 36. The fuel composition according to Claim 35, wherein the
32 aromatic ester of component (c) is a phthalate ester.
- 33
- 34

-38-

- 01 37. The fuel composition according to Claim 20, wherein the
02 R group on the aromatic ester of component (c) is alkyl
03 of 8 to 13 carbon atoms.
- 04
- 05 38. The fuel composition according to Claim 20, wherein
06 component (a) is a polyisobutetyl amine, wherein the
07 amine moiety is derived from ethylene diamine or
08 diethylene triamine, component (b) is polyisobutene,
09 and component (c) is a phthalate ester.
- 10
- 11 39. A fuel concentrate comprising an inert stable
12 oleophilic organic solvent boiling in the range of from
13 about 150°F to 400°F and from about 10 to 90 weight
14 percent of an additive composition comprising:
- 15
- 16 (a) a fuel-soluble aliphatic hydrocarbyl-substituted
17 amine having at least one basic nitrogen atom
18 wherein the hydrocarbyl group has a number average
19 molecular weight of about 700 to 3,000;
- 20
- 21 (b) a polyolefin polymer of a C₂ to C₆ monoolefin,
22 wherein the polymer has a number average molecular
23 weight of about 350 to 3,000; and
- 24
- 25 (c) an aromatic di- or tri-carboxylic acid ester of
26 the formula:
- 27
- 28
- 29
- 30
- 31
- 32
- 33
- 34
- 
- wherein R is an alkyl group of 4 to 20 carbon atoms, and x is 2 or 3.

-39-

- 01 40. The fuel concentrate according to Claim 39, wherein the
02 hydrocarbyl substituent on the aliphatic amine of
03 component (a) has a number average molecular weight of
04 about 750 to 2,200.
- 05
- 06 41. The fuel concentrate according to Claim 40, wherein the
07 hydrocarbyl substituent on the aliphatic amine of
08 component (a) has a number average molecular weight of
09 about 900 to 1,500.
- 10
- 11 42. The fuel concentrate according to Claim 39, wherein the
12 aliphatic amine of component (a) is a branched chain
13 hydrocarbyl-substituted amine.
- 14
- 15 43. The fuel concentrate according to Claim 42, wherein the
16 aliphatic amine of component (a) is a polyisobutetyl
17 amine.
- 18
- 19 44. The fuel concentrate according to Claim 42, wherein the
20 amine moiety of the aliphatic amine is derived from a
21 polyamine having from 2 to 12 amine nitrogen atoms and
22 from 2 to 40 carbon atoms.
- 23
- 24 45. The fuel concentrate according to Claim 44, wherein the
25 polyamine is a polyalkylene polyamine having 2 to
26 12 amine nitrogen atoms and 2 to 24 carbon atoms.
- 27
- 28 46. The fuel concentrate according to Claim 45, wherein the
29 polyalkylene polyamine is selected from the group
30 consisting of ethylene diamine, diethylene triamine,
31 triethylene tetramine and tetraethylene pentamine.
- 32
- 33
- 34

-40-

- 01 47. The fuel concentrate according to Claim 46, wherein the
02 polyalkylene polyamine is ethylene diamine or
03 diethylene triamine.
- 04
- 05 48. The fuel concentrate according to Claim 47, wherein the
06 aliphatic amine of component (a) is a polyisobut enyl
07 ethylene diamine.
- 08
- 09 49. The fuel concentrate according to Claim 39, wherein the
10 polyolefin polymer of component (b) is a polymer of a
11 C₂ to C₄ monoolefin.
- 12
- 13 50. The fuel concentrate according to Claim 49, wherein the
14 polyolefin polymer of component (b) is polypropylene or
15 polybutene.
- 16
- 17 51. The fuel concentrate according to Claim 50, wherein the
18 polyolefin polymer of component (b) is polyisobutene.
- 19
- 20 52. The fuel concentrate according to Claim 39, wherein the
21 polyolefin polymer of component (b) has a number
22 average molecular weight of about 350 to 1500.
- 23
- 24 53. The fuel concentrate according to Claim 52, wherein the
25 polyolefin polymer of component (b) has a number
26 average molecular weight of about 350 to 500.
- 27
- 28 54. The fuel concentrate according to Claim 39, wherein the
29 aromatic ester of component (c) is a phthalate,
30 isophthalate or terephthalate ester.
- 31
- 32 55. The fuel concentrate according to Claim 54, wherein the
33 aromatic ester of component (c) is a phthalate ester.
- 34

-41-

- 01 56. The fuel concentrate according to Claim 39, wherein the
02 R group on the aromatic ester of component (c) is alkyl
03 of 8 to 13 carbon atoms.
04
05 57. The fuel concentrate according to Claim 39, wherein the
06 component (a) is a polyisobutetyl amine, wherein the
07 amine moiety is derived from ethylene diamine or
08 diethylene triamine, component (b) is polyisobutene,
09 and component (c) is a phthalate ester.
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34

INTERNATIONAL SEARCH REPORT

Int. application No.
PCT/US95/04924

A. CLASSIFICATION OF SUBJECT MATTER		
IPC(6) :C10L 1/18, 1/22 US CL :044/389, 398, 412 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) U.S. : 044/389, 398, 412		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 5,296,003 (Cherpeck) 22 March 1994, see abstract.	1-57
A	US,A, 4,125,382 (O'Brien et al) 14 November 1978, see claim 1.	1-57
A	US,A, 3,660,056 (Dorsch) 02 May 1972, see Abstract.	1-57
A	US,A, 2,937,933 (Heisler et al) 24 May 1960, see claims 1-3	1-57
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <ul style="list-style-type: none"> *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier documents published on or after the international filing date *L* documents which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed <p>T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>Z document member of the same patent family</p>		
Date of the actual completion of the international search 13 JUNE 1995	Date of mailing of the international search report 12 JUL 1995	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer  JACQUELINE V. HOWARD Telephone No. (703) 308-2514	